FACULTY OF TECHNOLOGY

Kinetics of gasification of biochar made of Kraft lignin

Antti Tarkka

Master's programme of process engineering

Master's thesis

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Tiivistelmä
Opinnäytetyöstä Oulun yliopisto Teknillinen tiedekunta

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Työn nimi Kraft ligniinistä valmistetun biohiilen kaasuttamisen kinetiikka.			
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Tiivistelmä

Diplomityön tavoitteena on selvittää Kraft-ligniinistä valmistetun biohiilen kaasuuntumisen kinetiikkaa. Selvitetyn kinetiikan avulla saadaan kartoitettua biohiilen käyttäytymistä korkeassa lämpötilassa hapettomassa ympäristössä. Selvitetyillä ominaisuuksilla voidaan jatkossa tutkia ja kehittää mahdollisuutta korvata perinteistä metallurgista koksia esimerkiksi värimetallien valmistuksen yhteydessä, näin tehostamalla kuonan käsittelyä ja pienentämällä ympäristölle aiheutuvaa kuormaa.

Teoriaosassa käsitellään biomassaa ja siitä saatavaa Kraft-ligniiniä, mahdollisia käyttökohteita Kraft-ligniinistä valmistetulle biohiilelle sekä teoreettista pohjaa kaasuuntumisreaktion tutkimiselle. Teoriaosan tavoite on antaa kuvaa siitä, mitä biohiili on, missä käyttökohteissa sitä voitaisiin hyödyntää esimerkiksi värimetallien valmistuksessa, sekä millä tavoin biohiilen kaasuuntumista voidaan tutkia.

Kokeellinen osa sisältää biohiilinäytteiden valmistamisen sekä kineettisten parametrien selvittämisen biohiilinäytteille TGA-laitteiston avulla. Näytteistä saatu data sovitetaan sopivaan isotermiseen malliin, josta saadaan määriteltyä kaasuuntumisen kinetiikkaa kuvaavat parametrit.

Tutkimustyöstä selvitettiin kaikkien näytteiden aktivoitumisenergiat sekä nopeusvakiot. Kirjallisuuteen verrattuna saadut biohiilen arvot ovat melko pieniä, mutta tämä oli odotettavissa, materiaalin ja olosuhteiden johdosta. Tuloksista havaitaan, että Kraft-ligniini-pohjainen biohiili on hyvin reaktiivista esimerkiksi verrattuna perinteiseen metallurgiseen koksiin. Kraft-ligniinistä valmistetun biohiilen aktivoitumisenergia sai arvoja väliltä 6–19 kJ/mol riippuen pyrolyysilämpötilasta ja nopeusvakion arvoja väliltä 0,00262–0,00617 1/s. Koksilla vastaavat arvot olivat suuruudeltaan 80 kJ/mol ja 0,26503 1/s.

Kraft-ligniinistä valmistetun biohiilen käyttäminen pelkistimenä esimerkiksi värimetallien valmistuksessa on tulevaisuudessa mahdollista, mutta ennen sitä sen valmistuskustannukset ja tuotantoon liittyvät ongelmat olisi hyvä ratkaista.

Muita tietoja

Muita tietoja:

Abstract

For thesis University of Oulu Faculty of Technology

Degree Programme (Bachelor's Thesis, Master's Thesis)	Major Subject (Licentiate Thesis)
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Kinetics of gasification of biochar made of Kraft lignin

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Abstract

The aim of the thesis was to find out the gasification kinetics of biochar made from Kraft lignin. The studied kinetics can be used to map the behavior of biochar at high temperatures. In the future, the investigated properties can be used to study and develop the possibility of replacing traditional metallurgical coke, for example in the production of non-ferrous metals, thus improving the efficiency of slag treatment and reducing the burden on the environment.

The theoretical part focuses on the biomass and the Kraft lignin obtained from it, possible applications for biochar made from Kraft lignin and the theoretical basis for studying the gasification reaction. The aim of the theoretical part is to give basic information on what biochar is, in what applications it could be utilized and in which way the gasification of biochar can be studied.

The experimental part includes the preparation of biochar samples and the determination of kinetic parameters for the biochar samples using TGA equipment. The data obtained from the samples are fitted to a suitable isothermal model from which parameters describing the gasification kinetics can be determined.

From the research work we were able to find out the activation energies and velocity constants of all the samples. Compared to the literature, the values of biochar obtained are quite small, but this was to be expected, due to the material and conditions. The results show that Kraft lignin-based biochar is highly reactive, for example when compared to conventional metallurgical coke. The activation energy of biochar made from Kraft lignin got values between 6 and 19 kJ/mol depending on the pyrolysis temperature and the velocity constant values between 0.00262 and 0.00617 1/s. The corresponding values for coke were 80 kJ/mol and 0.26503 1/s.

The use of biochar made from Kraft lignin as a reducing agent, for example in the production of non-ferrous metals, is possible in the future, but before that its production costs and production problems should be solved.

Additional Information

Additional Information:

Foreword

This diploma thesis has been implemented in TOCANEM project between 22 February and 21 August 2021. The work was made in co-operation with Boliden Harjavalta and Boliden Kokkola. The thesis focuses on researching the kinetic properties of biochar made from Kraft lignin, which could possibly be utilized as a reducing agent in the future, e.g. in the treatment of side stream and residue of non-ferrous metals production.

I want to thank my work inspector Eetu-Pekka Heikkinen and my work supervisor Aki Koskela and Petri Sulasalmi, who together with Boliden Oy's instructors Justin Salminen helped to complete my thesis work with the help of excellent and comprehensive guidance. I would also like to thank the Process Metallurgy research unit at the University of Oulu and laboratory technician Tommi Kokkonen for their outstanding laboratory facilities and assistance in using the research equipment.

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In Oulu, 11.8.2021

Antti Tarkka

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Symbols and abbreviations used

A	amplitude of temperature
DSC	Differential scanning calometry
E	energy
E_A	activation energy
FTIR	Fourier Transform Infrared Spectroscopy
JMA	Johnson-Mehl-Avrami
k	reaction rate constant
k_0	law of pre-exponential factor
L	amplitude of weight change rate
L_0	pore length, cm/cm3
m	mass, kg
MW	molecular weight, g/mol
n	reaction order
R	gas constant
RPM	Random Pore Model
rpm	rounds per second
S_0	pore surface area, cm^2/cm^3
T	temperature
t	time
TGA	Thermo Gravimetric Analysis
URCM	Unreacted Shrinking Core Model
VM	Volume Model
Wt.%	mass percentage
α	phase fraction
ε_0	solid porosity
ψ	parameter of particle structure

1 INTRODUCTION

Managing and reducing carbon emissions plays a significant role in sustainable development, both economically and environmentally. It is important that in the future we are able to use carbon in industry without increasing the total amount of coal in the global carbon cycle. To achieve this, the reduction of traditional carbon sources such as coal is critical.

Coke used in metallurgical processes is one of the major carbon-emitting raw materials used extensively in industry, e.g. as a reducing agent. Replacing metallurgical coke with biochar would significantly reduce the need to use non-renewable as a raw material of coke, which would reduce the release of fossil carbon into the carbon cycle and make it easier to control carbon emissions. However, research of biochar for industrial use is relatively new research topic.

In order to implement the use of biochar in industry, its properties must be well known. However, these properties vary depending on the biochar feedstock to its production methods. One of the most promising raw materials for biochar is Kraft lignin, from which biochar could be produced by pyrolysis.

The aim of this work is to investigate kinetics of gasification of biochar made from Kraft lignin, which can be used to predict the behavior of biochar in different industrial environments. The study of the gasification kinetics is performed using thermogravimetric analysis (TGA) equipment. The data obtained from the equipment are fitted to an isothermal model suitable for the experiment, from which an Arrheinius plot is formed. Using the Arrhenius graph, the desired gasification parameters can be generated.

2 BIO-BASED CARBON

2.1 Biomass

Biomass is renewable organic material derived from living or recently living organisms that can be used as an energy source. Biomass includes e.g. wood, manure, various plants, food scraps, animal fats and household waste. Biomasses can be classified into five different categories, corpses, alcohol fuels, landfill gases, garbage's, and woods. For example, the category of wood includes e.g. firewood, sawdust, logs and in general all the wood processing wastes.

There are many ways to convert biomasses to useful energy. Biomass conversion can be done by direct combustion, thermochemical conversion, chemical conversion or by biological conversion. Direct combustion produces heat and is the most common method to produce energy from biomass. Thermochemical conversion produces solid, gaseous, and liquid fuels by using pyrolysis or gasification. Chemical conversion is used to convert oils, animal fats and greases into fatty acids that are utilized for production of biodiesel. Biological conversion includes methods such as fermentation and anaerobic production methods to produce ethanol and natural gas. In order to recover energy from biomass as efficiently as possible, its conversion to energy must be viewed in terms of raw material. For example, because wood-based raw material contains a lot of lignin, its thermochemical conversion is much more efficient compared to, for example, biogenic materials such as wool and food waste. The lignocellulose content has a significant impact on the energy efficiency of biomass and its applications. (U.S. Energy Information Administration (EIA) 2020)

2.2 Lignocellulosic biomass

Lignocellulosic biomass or lignocellulose is plants dry material that is composed of carbon hydrate polymers like cellulose and hemicellulose and aromatic polymers like lignin. Carbohydrate polymers contains different sugar monomers which are tightly bound to lignin that works as a supporting structure. Cellulose, hemicellulose, and lignin are not uniformly distributed within the cell walls and the quantity and structure is dependent on the species, tissues, and maturity of the plant cell wall. Lignocellulosic biomass normally consists of 35–50% cellulose, 20–35% hemicellulose, and 10–25%

lignin. Table 1. shows the cellulose, hemicellulose and lignin content of different species of lignocellulosic biomass. (Isikgor and Becer 2015)

Table 1. Types of lignocellulosic biomass and their chemical composition. (Isikgor and Becer 2015)

Lignocellulosic biomass		Cellulose (%)	Hemicellulose (%)	Lignin (%)
Hardwood	Poplar	50.8–53.3	26.2–28.7	15.5–16.3
	Oak	40.4	35.9	24.1
	Eucalyptus	54.1	18.4	21.5
Softwood	Pine	42.0–50.0	24.0–27.0	20.0
	Douglas fir	44.0	11.0	27.0
	Spruce	45.5	22.9	27.9
Agricultural waste	Wheat Straw	35.0–39.0	23.0–30.0	12.0–16.0
	Barley Hull	34.0	36.0	13.8–19.0
	Barley Straw	36.0–43.0	24.0–33.0	6.3–9.8
	Rice Straw	29.2–34.7	23.0–25.9	17.0–19.0
	Rice Husks	28.7–35.6	12.0–29.3	15.4–20.0
	Oat Straw	31.0–35.0	20.0–26.0	10.0–15.0
	Ray Straw	36.2–47.0	19.0–24.5	9.9–24.0
	Corn Cobs	33.7–41.2	31.9–36.0	6.1–15.9
	Corn Stalks	35.0–39.6	16.8–35.0	7.0–18.4
	Sugarcane Bagasse	25.0–45.0	28.0–32.0	15.0–25.0
	Sorghum Straw	32.0–35.0	24.0–27.0	15.0–21.0
Grasses	Grasses	25.0–40.0	25.0–50.0	10.0–30.0
	Switchgrass	35.0–40.0	25.0–30.0	15.0–20.0

Lignocellulose can be roughly classified into three different categories, virgin biomass, waste biomass and energy crops. Virgin biomass includes all naturally occurring terrestrial plants for example trees, bushes, and grass. Waste biomass is a low value byproduct of various industrial sectors such as agriculture and forestry. Energy crops contain ahigh yield of lignocellulosic biomass that can be used for instance as a raw material to produce second generation biofuels. (Isikgor and Becer 2015; Biocore n.d.)

In pulp and paper industry, lignocellulosic biomass is used as a feedstock in pulping process where lignin and cellulose are separated. The cellulose is used in the paper industry and the separated lignin can be recovered for other uses for example to produce biochar. There are different industrial ways to produce lignin. In 2019, the lignin market size exceeded 730 million dollars and it is expected to grow annually 5.7 % between 2020 and 2026. The growth of the lignin market comes mainly from as a dispersant in Agrochemical production and end-use applications for example coating, painting and cleaner products. However lack of consumer awareness regarding the benefits of using biobased material like lignin and forest conservation initiatives may slow down market growth. (Kunal, Ahuja; Kritika 2020; Isikgor and Becer 2015; Biocore n.d.)

2.3 Lignin and industrially prepared lignin

Lignin is a complex organic polymer which is an important structural support in cell walls of most plants. The lignin fills the cell wall spaces between the components of cellulose and, hemicellulose. Lignin is a branched polymer that does not have a single specific structure. Lignin is composed of three different main types of lignols, which are the starting materials for the biosynthesis of lignans and lignin. These three binds to each other in a number of different ways forming a long chemical structure. Figure 1. shows one known polymeric form of lignin. (Boerjan, Ralph, and Baucher 2003)

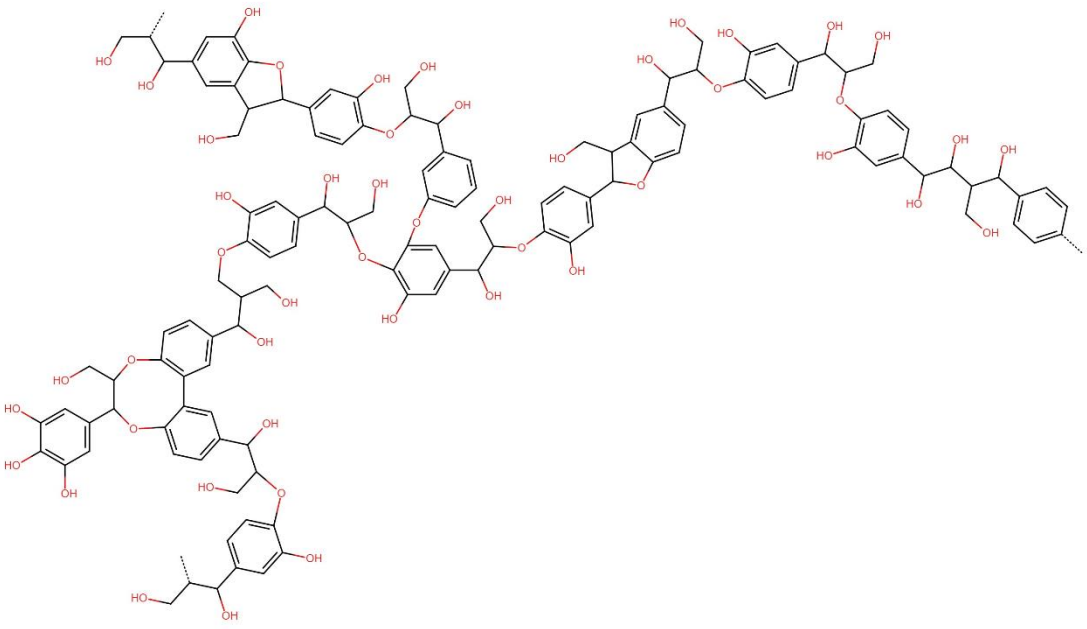

Figure 1. An example of the chemical structure of lignin from wood.

Different processes and treatments produce different types of lignin. For example, pulp cooking can be performed by four different methods and the lignin by-products produced by these methods are different from each other. For example, Kraft pulping produces Kraft lignin, sulfite pulping produces lignosulfonate, alkali pulping produces alkali lignin and organic solvent pulping produces organic solvent lignin. Of these, the Kraft pulping is the most common ways to produce lignin. (Isikgor and Becer 2015)

2.4 Kraft lignin

Kraft lignin is industrial lignin obtained from Kraft pulping. Kraft pulping is an important method for converting coniferous wood to pulp because its yield is higher than other alkaline pulping methods. Kraft pulping account for about 85% of the total lignin production in the world. Kraft lignin typically contains around 64 wt.% of carbon, 25 wt.% of oxygen, 5.4 wt.% hydrogen, 1.4 wt.% sulfur and 0.11 wt.% nitrogen. In Kraft lignin process 90-95% of the lignin is dissolved into the alkaline cooking liquor that contains sodium hydroxides and sodium sulfides where the lignin macromolecules are fractured and molecular weight decrease. (Isikgor and Becer 2015; H. Chen 2015)

2.5 Biochar from Kraft lignin

Biochar made from Kraft lignin is coal-like substance that is generated by thermochemical conversion in a low oxygen environment. The chemical and physical properties of the raw materials greatly affect the formation of the biochar. Biomass that contains more lignin and less cellulose produces a high yield of biochar, but also higher lignin content increases the porosity of biochar. Today, Kraft lignin is mainly burned in the production of heat and electricity. In the future, a better option could be further thermochemically processing it into biochar, thus increasing the value of lignin as a raw material. (Laurila 2019)

Biochar can be produced in five different ways on an industrial scale. These include fast, medium, slow and-, flash pyrolysis and gasification method. The difference between these is the processing time and temperature, which results in different amounts of biochar, biofuel and gases. Different pyrolysis methods and product yields

obtained with dry wood raw material is shown in Table 2. Most common way in biochar production is to use slow pyrolysis, i.e. so-called carbonation. The temperature of slow pyrolysis is usually around 300-600 °C and the residence time in pyrolysis is several tens of minutes, sometimes even hours. The yield of solid charcoal in slow pyrolysis is around 30-50%, which is the highest solid yield of the pyrolysis methods. About 300-500 kg of biochar is obtained from 1000 kg of dry wood. In addition to charcoal, pyrolysis produces pyrolysis liquids containing hydrocarbons and organic acids, as well as non-condensable gases such as carbon monoxide and hydrogen. About 25-30% of pyrolysis liquids and about 30-35% of non-condensable gases are formed, depending on the reaction conditions and raw materials. (Laurila 2019; Suomen Biohiiliyhdistys 2021; Spliethoff; 2012; Hakala et al. 2019)

By influencing the reaction conditions, the quality and yield of the final products can be significantly affected. However, the process is energy intensive, which is why about 20% of the wood is used to maintain the process. In addition to the high energy requirement, major investments include investments in equipment and materials prices. (Laurila 2019; Suomen Biohiiliyhdistys 2021; Spliethoff; 2012; Hakala et al. 2019)

Table 2. Processing temperatures and times of different pyrolysis methods and product yields obtained with dry wood raw material. (Laurila 2019)

Pyrolysis method	Reaction conditions		Products		
	Temperature (°C)	Processing time (s)	Biochar (%)	Bio-oil (%)	Gas (%)
Fast	575-975	0,5-10	12	75	13
Medium speed	500	10-20	20	50	30
Slow (carbonation)	275-645	45-550	35	30	35
Flash	775-1 025	<0,5	20	50	30
Gasification	625-1225	10-20	10	5	85

2.6 Structure of biochar

It is important to know the composition and structure of the biochar when considering its uses. Biochar effects in a process can be beneficial or detrimental depending on its properties. Physical structure is heavily involved in reactivity of biochar. The larger the number of pores, the larger the surface area and, as a result, the reaction surface area

increases. Therefore, higher porosity of char makes a biochar more reactive. The particle size also effects the reactivity of the biochar. The smaller the particle size the larger the total surface area of the char and therefore it is more reactive. In addition to this the structure of biochar is also highly dependent on the processing temperature. At temperatures lower than 100 °C, the biomass does not change much, only the volatile materials like moisture starts to evaporate and some heat sensitive substances can start to break down for example vitamin C and proteins. When temperature reaches around 100 °C or slightly higher all remaining water has been evaporated or been absorbed into the material and the breakdown of organic molecules start to occur. At the temperature of 160-180 °C most of the sugars begin to break. The main components in wood materials like cellulose and lignin starts to break down at temperature of 350 °C however the decomposition of lignin continues up to the 500 °C. As the temperature rises, the carbon structure of biochar changes. Carbon structure of biochar can be divided into four different categories according to the manufacturing temperature: transition-, amorphous-, composite- and turbostratic (carbonized) biochar. In transition biochar the organic macromolecules (e.g., lignin, hemicellulose, and cellulose) are lost and single ring aromatic compounds are formed. In amorphous biochar identifiable biopolymers have disappeared and aromatic compounds of two and three rings have formed. In composite biochar a combination of amorphous biochar and aromatic ring stacks of 3 to 5 carbon layers are starting to form. In turbostratic biochar, all amorphous biochar is either evaporated or converted to aromatic rings. However, biochar rarely achieves the turbostratic state because it would require a prolonged processing time in pyrolysis or a temperature above 700 ° C. (Laurila 2019; Spliethoff 2012)

2.7 The benefits of pyrolysis

Pyrolysis is a thermochemical conversion method in which the organic components are decomposed as a result of heating in the absence of air/oxygen. Pyrolysis is done either in a vacuum or an inert atmosphere such as nitrogen atmosphere to displace oxygen. Pyrolysis is reaction that breaks down macromolecules, esters, amides and separates small molecules. Most common pyrolysis products are coke, tar and charcoal. Other products obtained by pyrolysis include water, carbon monoxide, various hydrocarbons, acetic acids, methanol, ammonia, phenols and organic products. The advantage of pyrolysis is cleaner product, higher energy density of the material obtained from the process and various differentiated by-products that can be further processed. The

disadvantages are high energy demand and harmful gases released in the pyrolysis reaction, which can be challenging to handle. (Zhou et al. 2013)

2.8 Availability of biochar

The availability of lignin-based biochar is growing in Finland, but so far it can still be challenging to produce large quantities of biochar at a competitive price. For example, biomass transport, handling and efficient pretreatment methods are major problems which reduce the profitability of lignin-derived biochar. The availability of lignin-based biochar depends on several factors, such as the price of the raw materials, processing costs, the amount of emissions taxes, and the transportation costs. (Kunal, Ahuja; Kritika 2020; Hakala et al. 2019; Yamamoto 2018)

There are several different sources of biocarbon to be produced in Finland, but its profitability is still questionable. However, profitability is expected to improve in the future due to rising emissions taxes and increasing demand. One way to ensure the availability of biochar is to produce the biochar itself on site from a lignin-based raw material. For example, the St1 Biofuels Cellunolix® bioethanol plant in Kajaani produces 15,000 tonnes of dry lignin annually and intends to operate in new industrial areas, allowing annual lignin production to reach close to 100,000 tonnes per year, which could produce about 22,500 tonnes of biochar per year. Another option is to buy ready-made biochar, for example, from the biorefinery plants, which would have an annual biochar production of around 20,000 tonnes. However, the most economically viable way to produce biochar is with a pulp mill, which means that the availability of biochar can potentially be as high as 95,000 tonnes per year. (Hakala et al. 2019; Yamamoto 2018)

3 USE OF BIOCHAR IN NON-FERROUS METALS PRODUCTION

3.1 Non-ferrous metal production

Nickel, copper and zinc are one of the most common non-ferrous metals. Non-ferrous metals are normally more expensive than ferrous metals and are produced by using electrolysis.

In electrolysis process the non-ferrous metal like zinc, nickel and copper are often produced by using electric current to drive an otherwise normally non-spontaneous chemical reaction. In the manufacture of different non-ferrous metals, various residues side streams can be formed. Most common way of managing these iron containing residues and wastes is landfilling. Minimizing of these waste amounts and recovered metals values would contribute into sustainability and into circular economy. Also, utilization of the wastes by producing raw materials for different industries like the road and concrete industries can bring financial gains. In general, the recovery and utilization of the residues can be improved by recovering residual volatile metals from the slag using a reduction reaction. The slag is reduced typically by using carbonaceous materials such as anthracite metallurgical coke, coke powder or coal. The purpose of adding the reducing agent in the pyrometallurgical process is to reduce volatile metals for recovery and cleaning of the slag. When performed correctly, reduction can enable the recovery of valuable metals or, for example, the separation of harmful materials, whereby e.g. process efficiency is improved, less waste is generated, and utilization of residue is facilitated. Biochar could be utilized in several non-ferrous metal slag treatment processes, such as nickel, copper, and zinc.

Today, traditional metallurgical coke, made by dry distillation of coal, is mainly used for the reduction. However, coke is a natural resource classified as non-renewable and has a large carbon footprint and the aim is to reduce its use in the future. To replace coke, the biochar is considered to be a good alternative, which has a much smaller total carbon footprint than coke because it is renewable natural resource. The use of biochar also reduces the need for coal mining, which in itself saves the environment and also reduces significant amounts of fossil carbon entering the carbon cycle.

3.2 Use of biochar in the manufacture of nickel

The nickel ore pentlandite $(Ni, Fe)_9S_{16}$ is commonly used in the nickel production process. After drying the ore is fed to a flame melting furnace to form a so-called nickel rock (matte) and nickel slag. The matte contains around 55-60% nickel and nickel slag containing around 2-6 % nickel. (Heikkinen and Heino 2002)

The separation of matte and slag takes place in a flame smelting furnace due to differences in density. The denser matte settles at the bottom of the lower furnace, from where it is moved into water-based granulation and to further purification. Nickel slag is sent to an electric furnace for further processing. (Härkönen 2010)

Because nickel slag contains significant amounts of valuable nickel, as well as other precious metals belonging to the platinum group, it is economically viable to purify the slag by a reduction process. (Heikkinen and Heino 2002)

Traditionally, the reduction process is carried out in a batch style by adding nickel slag to the furnace that is pre-charged with metallurgical coke, whereby the slag initiates reduction so that nickel, precious metals and worthless components separate into their own phases in the matte, as well as in the slag. (Härkönen 2010)

In the production of nickel, the metallurgical coke could be partially or completely replaced by biochar, which would significantly improve the environmental friendliness of the process, the fossil carbon footprint and the availability of the reducing agent. (Heikkinen and Heino 2002; Härkönen 2010)

3.3 Use of biochar in manufacture of copper

Copper manufacturing also produces slag, in the production of other non-ferrous metals. However, in current Finnish copper production, carbon is not necessarily used in slag treatment because of the use of the floating process. (Heikkinen and Heino 2002)

In the production of copper, the enriched copper ore is smelted in a flash furnace to form two different phases, a copper matte and a slag phase where the lighter slag phase is directed to the slag treatment and the heavier copper matte to the copper production. (Heikkinen and Heino 2002)

In slag treatment, the slag is periodically poured into ladles and allowed to cool down. If the sulfur content of the slag is high enough in the cooling stage the copper trapped in the slag begins to settle downward before solidification, forming larger copper droplets. After cooling, the slag is treated by crushing it into a fine crush, whereby copper can be separated from the slag using a foaming process. The slag concentrate from the foaming process is recycled back to the flame in the furnace. The copper content of the waste slag after treatment is around 0.25%. However, this crushing process is very energy intensive and enables the slag to become soluble. In some cases, instead of flotation, the reduction of copper slag can be carried out in an electric oven by using coke. (Heikkinen and Heino 2002)

The slag treatment of the copper process could be developed more in the same direction as, for example, the slag treatment of nickel processes. In which case, the slag produced in the manufacture of copper would be done by using reduction reaction with biochar, thus saving energy-consuming mechanical crushing and the problematic solubility. This could be done for example using Isasmelt technology where biochar could act as a reducing agent and a fuel. Isasmelt uses submerged lance injection technology to provide highly efficient mixing of feed materials in a molten slag bath where off gases are collected from the top and the molten products from the bottom of the furnace. (Heikkinen and Heino 2002; Key to Metals AG. 2015)

3.4 Use of biochar in manufacture of zinc

In zinc production during the roasting process zinc oxides can react with iron impurities and form zinc ferrites that cannot be dissolved in diluted sulfuric acid solution in the leaching process. This leads to lower zinc leaching rate and increased amounts of zinc in the leaching residue. To prevent this from happening iron is usually precipitated from acid leach solutions as jarosite or goethite. Usually, significant amounts of jarosite and some of goethite residues are recovered from the process. In zinc production jarosite process can generate between 0.5-0.9 tons of dry jarosite per ton of produced zinc. In addition to the amount produced, one challenge is that the impurities produced in addition to jarosite may include, for example, base metals such as Zn, Pd, Cu, critical elements like In Ga, Ge, Sb, precious metals Ag, Au and problematic elements such as As, Cd, Hg. Due to different impurities, it is common that the residues are not further processed but are stored without further treatment. At the time there is no economically

feasible way to deal with the residues. However, there is an interest in exploring the possibility of processing this residue into a more useful forms such as raw materials for the construction industry, and at the same time, recovering the valuable metals from the residue. This could be done by using pyrometallurgical treatment of jarosite leach residue for example with Ausmelt treatment. (Heikkinen and Heino 2002; Montanaro et al. 2001; Zhang et al. 2019)

The aim of the Ausmelt treatment is to recover as much zinc and lead as oxidation fume as possible. In the Ausmelt treatment, the smelting of zinc residues is carried out in the presence of reductant coal, whereby oxide fumes and slag are generated. In order to achieve the lowest possible zinc content (about 1%) in the slag, the pyrometallurgical treatment should be carried out in two different steps. The first step is smelting/oxidation which is implemented at temperature of 1250 °C. The second step is reduction which is carried out at 1300 °C. The fumes from both steps containing zinc oxides (ZnO) are directed back to the dissolution step where the zinc can be reused. In the Ausmelt process, the reducing carbon has been found to reduce the concentration of zinc and lead in the slag, together with oxidative treatment, thus improving the efficiency of the process. Normally, a metallurgical coke is used as the reducing agent because it can withstand the process conditions and also acts as a fuel in the process. (Heikkinen and Heino 2002; Montanaro et al. 2001; Zhang et al. 2019)

In Ausmelt process biochar could be an interesting option to replace fossil coke because of its major advantage in renewability and lack of fossil carbon. (Heikkinen and Heino 2002; Montanaro et al. 2001; Zhang et al. 2019)

3.5 Challenges of biochar in non-ferrous metals production

Biochar will need more studies before it can be fully replacing the coke. The attributes of biochar or process conditions may need to be improved to fit specific properties of biochar before it can be used in order to maximize its efficiency. Bio-based reducing agent is much more reactive than metallurgical coke and this can be problematic at high temperatures, as biochar may start burn even before it encounters the slag to be reduced. This can be prevented by feeding the reducing agent directly into the substance to be reduced by means of a lance. High reactivity may also cause slag foaming, which must be considered in the process. In addition to high reactivity, the low density of bio-based

reducing agents can also be problematic, as it does not come into proper contact with the slag, resulting in a low amount of oxidation. To prevent this from happening the density problem could be solved by agglomerating the reducing agent into pellets or briquettes, increasing the density of the bio-based reduction agent. Compared to traditional coke, biochar is also much more difficult to store if it is not in briquette or pellet form, as it is very fine-grained and highly flammable. Therefore, its storage conditions should be reviewed to minimize the risk of its spread and ignition.

4 STUDY OF GASIFICATION REACTION

4.1 Thermogravimetric analysis

The isothermal method can be used to study the gasification reactions in different gas atmospheres. This can be studied in practice using thermal gravimetric analysis (TGA). TGA is a thermo-analytical technique that measures the weight changes of a sample at a given time and temperature. TGA provides quantitative and qualitative information about physical changes in the sample in response to the temperature, atmosphere, and the heating rate. The TGA can be used to quantify the major constituent of a material, study decompositions and thermal stability, and be used as a secondary means of material identification. (NETZSCH Instruments North America LLC 2019)

The TGA subjects a small sample of material to a temperature and atmosphere and measures the weight changes of the sample. The most common TGA experiment involves heating the sample to high temperatures so that the organic matter of the sample decomposes. (NETZSCH Instruments North America LLC 2019)

In TGA the sample is placed onto a sample holder that is measured by a scale inside a sealed furnace with equipped thermocouple that measures temperature. In the experiment the sample is heated at the specific rate that can be chosen for example 25 °C per minute to desired temperature for example to 700 °C. The range of maximum and minimum heating rate and temperature is specific to a kinetic model used in the TGA during the tests. During this heating ramp the weight of the sample and the temperature is measured. This data then is recorded as a function of temperature or time. Additionally, the controllable gas atmosphere inside the furnace enables e.g. oxidizing or reducing gas atmosphere.(NETZSCH Instruments North America LLC 2019)

One of the most common uses of TGA is quantification of the individual formulation constitution for example in reverse engineering plastics or comparison of materials. TGA is also used for assessment of a thermal stability like decomposition behavior and compositional changes such as degradation. (NETZSCH Instruments North America LLC 2019)

TGA has some limitations which are good to be consider when used. Because of relatively small sample of material in some cases, the sample does not give an overall picture of the material. Dynamism of the tests must also be considered. Tests with too high dynamism may give inaccurate results but on the other hand low dynamism gives more accurate results but takes longer to implement. It is also important to make sure that no contamination occurs in the TGA equipment during the preparation of the samples, as this may significantly affect the results of the tests and this can be hard to detect. Also, in TGA the different parameters will yield different results. This means that TGA curves are not Fingerprint curves. When parameters are different the general shape of the curves will change. Another consideration of TGA is that it is limited to quantification of the major parts of the material. Small amount of formulation constituents cannot typically be quantified. Also, if the material contains multiple constituents that decompose over similar temperature ranges the weight losses can overlap making quantification of separate constituents difficult. Finally, TGA is only a secondary way to identify different materials. If the material is unknown, it may be necessary to run more tests such as Differential Scanning Calorimetry (DSC) or Fourier Transform Infrared Spectroscopy (FTIR). (Dai et al. 2020; NETZSCH Instruments North America LLC 2019; Salin and Seferis n.d.; Spliethoff; 2012)

4.2 Kinetic models of TGA

Modulated TGA Equation is used for gathering the kinetic profiles from modulated TGA. The modulated TGA uses a Fourier transform process to gather information over the complete process of the temperature program. The parameters that are needed to be gathered includes the half amplitude of the temperature oscillation (A) and the logarithm of the reaction rate, that corresponds to the peak and the valleys of the oscillatory derivative signal (L). If sinusoidal temperature oscillation has been used, the derivative of the oscillation is also a smooth continuous function, and this permits the Fourier transform. It is also possible to perform the test with Brian Dickens and Joe Flynn’s manner as a factor jump method by using stair step profiles. (TA Instruments 2015)

Modulated TGA Equation is presented in equation (1):

$$E_A = \frac{R(T^2 - A^2)L}{2A} \quad (1)$$

Where E_A = activation energy, R = gas constant, T = temperature, A = temperature (half) amplitude, L = amplitude of ln(weight change rate). (TA Instruments 2015)

In TGA work, an analytical kinetic model is selected depending on the sample and the desired data. Commonly used TGA kinetic methods are Single heating rate method, Variable heating rate method, Modulated temperature method and Isothermal method. In TGA kinetics these can be applied for example to study materials Thermal stability, drying or lifetime estimations. (TA Instruments 2015; The Madison Group 2020)

4.2.1 Single heating rate method

Single heating rate method has the advantage of a simple calibration, it has only single sample, the experiment can be done rapidly, and it can provide all three kinetic parameters, activation energy (E), law of the pre-exponential factor (k_0) and reaction order (n). Single heating rate method is however not common because it has some drawbacks. It can only be used in reactions that are well-behaved. This means that the thermal curves need to be smooth, continuous without any bumps or diddles. Also, the single experiment determinations are often fraught with experimental uncertainty in comparison to having a replicated determination. This may lead to poor reliability and it is normally applicated to nth order reactions and not for auto catalytic reactions. On the thermo gravimetry, the derivative signal is taken to make the determination and depending up on the filtering of the signal this can be inaccurate to some extent. (TA Instruments 2015)

4.2.2 Variable heating rate method

Variable heating rate method is applicable to complex, multi-staged reactions. This is major advantage because any portion of the reaction curve can be examined by the variable heating rate method. It provides activation energy (E) directly and if reaction order is assumed, the pre-exponential factor (k_0) can be determined. Variable heating rate method has very good reliability and can be performed manually if needed. Disadvantages are that the calibration process is lengthy, it requires at a minimum at

least four experiments and the assumption of reaction order may not be possible in some cases. If you want to have accurate data, many experiments are required, and this will take time to complete. (TA Instruments 2015)

4.2.3 Modulated temperature method

Modulated temperature method is the most common type of methods because it has less disadvantages compared to others. The calibration is simple, it has only single rapid experiment, the determination of activation energy (E_A) is model-free but first order reaction can be assumed to get logarithm of the pre-exponential factor (k_0). In this method the point of the reaction curve can be selected where the reaction is stable and thereby point of constant conversion can be known. Modulated temperature method is thought to be the most precise of the non-isothermal methods. Only disadvantages are the single experiment in which case it may be difficult to detect the error and assumption of the first order. (TA Instruments 2015)

4.2.4 Isothermal methods

Isothermal methods have advantages of being able to apply several different mathematical models to the treatment of data and to be used to determine kinetic parameters like nth order and auto catalytical reactions. This method provides information about activation energy (E_A), pre-exponential factors (k_0) and reaction orders (n) and (m). Isothermal methods are thought to be one of the most reliable methods for determination of reaction kinetics. (TA Instruments 2015)

Disadvantages for the Isothermal methods are that the reactions do not go to completion and because of this there is some imprecision in the total amount of the reaction time. Also, since they are performed isothermally experiment times are long and can take up to a day to perform for each sample and there must be at least four experiments so that reliable data can be achieved. Therefore, it may take up to a week to complete the experiments depending on the number of tests. (TA Instruments 2015)

4.2.5 Selecting the method

When selecting the appropriate method, the first step is the determine whether the reaction is nth-order or autocatalytic reaction. The second step is to determine what type of data is desired to be collected. What is the desired accuracy, whether the ease of

calculations and speed of the tests matter, etc. TA instruments have developed a flow chart presented in Figure 2. that helps to assess which method might be suitable with which type of reaction. (TA Instruments 2015)

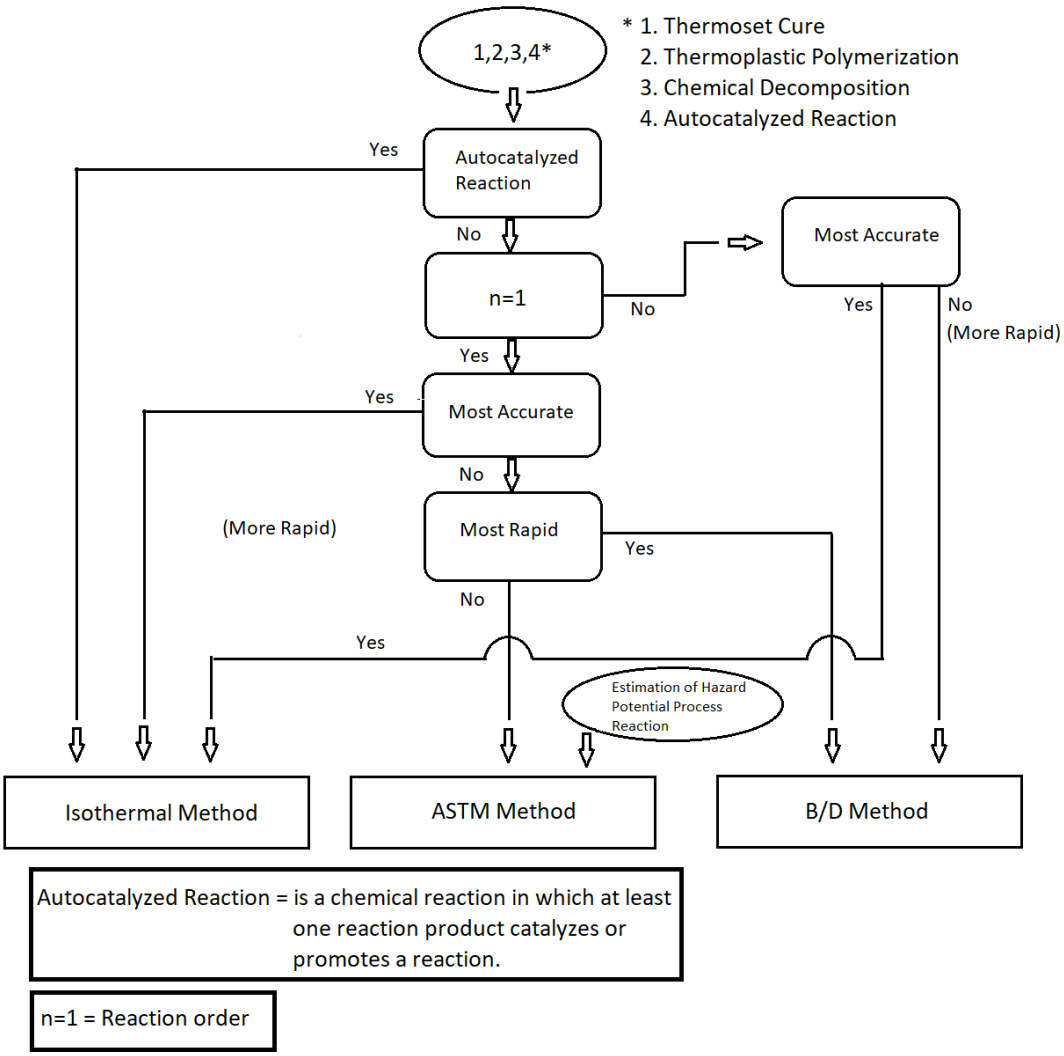

Figure 2. Method selection. Image modified from: (TA Instruments 2015)

4.3 Kinetic models of isothermal method

The isothermal method has several models modeling gasification. These models can be divided into theoretical and semi-empirical models. The most well-known theoretical models are the random pore model (RPM), the unreacted shrinking core model (URCM), and the volume model (VM). The unifying factor in the models is that if the partial pressure in the gas phase remains constant during the process, the apparent reaction rate constant is dependent on the temperature and in this case the Arrhenius

equation can be used. Arrhenius equation describes the temperature dependence of the rate constant of a chemical reaction, which can be represented in equation (2):

$$k = k_0 e^{-\frac{E_A}{RT}} \quad (2)$$

Where k_0 is the pre-exponential or frequency factor, E_A is the activation energy and R is the universal gas constant.

Contracting cylinder model (CCM) assumes that the sample is cylindrical in shape which shrinks as the reaction proceeds. Contracting cylinder model can be described in equation (3):

$$\frac{da}{dt} = kp(2(1-\alpha)^{\frac{1}{2}}) \quad (3)$$

Where a is gasification fractional conversion, α is the kinetics mechanism function in gasification reaction and p is the partial pressure of carbon dioxide.(Vyazovkin et al. 2010)

Random pore model (RPM) takes the pore structure and its evolution during the reaction into account. When gasification is under control of chemical reactivity, gasification rate can be described in equation (4):

$$\frac{da}{dt} = k_{RPM}(1-\alpha)\sqrt{1-\psi \ln(1-\alpha)} \quad (4)$$

where, a is gasification fractional conversion, α is the kinetics mechanism function in gasification reaction and ψ is parameter of particle structure that is described in equation (5)

$$\psi = \frac{4\pi L_{0(1-\varepsilon_0)}}{S_0^2} \quad (5)$$

where ψ is the parameter of particle structure, S_0 is the pore surface area (cm2/cm3), L_0 the pore length (cm/cm3) and ε_0 is the solid porosity. (Farjas and Roura 2006)

Unreacted shrinking core model (URCM) assumes that the reaction initially occurs at the external surface of char and gradually moves inside. At the intermediate conversion of the solid, there is a shrinking core of non-reacted solid. The reaction can be described in equation (6):

$$\frac{da}{dt} = k_{URCM}(1-\alpha)^{\frac{2}{3}} \tag{6}$$

Where a is gasification fractional conversion and α is the kinetics mechanism function in gasification reaction.

Volume model (VM) does not consider the structure changes of char during gasification, assuming that the gasifying agents react with char at all active sites, which are uniformly distributed on both the outside and inside particle surface. The rate expression can be described in equation (7):

$$\frac{da}{dt} = k_{VRM}(1-\alpha) \tag{7}$$

Where a is gasification fractional conversion and α is the kinetics mechanism function in gasification reaction.

Johnson–Mehl–Avrami (JMA) is one of most useful models used to evaluate the volume fraction of new phase transformed in the heating or cooling process. The nucleation and growth kinetics can be described in equation (8):

$$\frac{da}{dt} = (m+1)k(1-\alpha) * (-\ln(1-\alpha))^{\frac{m}{m+1}} \tag{8}$$

Where α is the transformed phase fraction, k is Arrhenius equation and m+1 is known as Avrami's exponent describes how that solids transform from one phase to another at constant temperature. (Farjas and Roura 2006)

When comparing JMA, RPM, URCM and VM models, the RPM model should be most fitting for studying gasification of biochar because it can give a better description about biochar in non-isothermal and isothermal gasification process. In isothermal gasification process, the phenomenon where conversion rate firstly increases and then decrease can only be observed by using RPM model. (Wang et al. 2015)

4.4 The most suitable kinetic model for the experiment

In the traditional kinetic analysis, the base is on fitting data obtained from the tests to the reaction models. The problem with model fitting method is that it is unable to determine the reaction model individually. This makes difficult to obtain reliable mechanical results even from isothermal data. On the other hand in non-isothermal method if the data from the test is fitted to the reaction models it will result highly uncertain values for Arrhenius parameters. Because of that the parameters cannot be compared with isothermal values. The most suitable kinetic mode is the isothermal method where the data can be easily fitted to the reaction models and from the models a reliable Arrhenius parameter can be obtained. (Vyazovkin et al. 2010)

When studying the kinetics of gasification, it can be stated that isothermal method is suitable method for the studies of the gasification of biochar by using flow chart presented in Figure 2. Even if the gasification reaction of the biochar is not autocatalyzed reaction and it has reaction order of one (n=1), we strive to achieve as accurate research results as possible. One of the most accurate data can be accrued by using isothermal method. And because of this isothermal method is one of the most sensible method that can be used in conducting studies with gasification reaction. (Vyazovkin et al. 2010)

The best isothermal model to describe gasification can only be determined once the data has been obtained from the TGA studies and can be fitted to the different models. There are many models that can describe gasification comprehensively and before any of the data was obtained the URCM and the VM were promising. However, once the data was obtained and adapted to different models, the CCM was concluded to be the most fitting model. Other well fitted models where Power law, One-dimensional diffusion and Contracting sphere. The choice of models is described in more detail in Chapter 5.4.1.

5 EXPERIMENTS

5.1 Preparations

The raw material used in this study is a purified Kraft softwood lignin (UPM BioPiva™ 300) manufactured by UPM Biochemicals. The Kraft lignin is non-toxic bio-based material from fully renewable sources. It can be used in various applications for example in combustion for generating power and heat or for replacing fossil-based materials like coke without compromising the performance. In Table 3. the typical features of UPM BioPiva™ 300 are presented.

Table 3. Typical features of UPM BioPiva™ 300.

Specification	Typical value
Appearance	dark brown powder with large agglomerates
Solid content 105 °C, %	63
Molecular weight Mw, g/mol	6000
Ash content 700 °C,%	<2
Storage stability, 20 °C	3–6 months

Figure 3. shows BioPiva™ 300 Kraft lignin powder before drying. The moisture content of Kraft lignin is around 35%.

Figure 3. BioPiva™ 300 Kraft lignin.

5.1.1 Kraft lignin drying

The first step for preparation of study samples is drying the Kraft lignin to lower its moisture content. The moisture content of UPM BioPiva ™ 300 Kraft lignin obtained from UPM Biochemicals was around 35%. Drying is done according to standard of SFS-EN 16179, where the material is applied in a layer not more than 2-3 cm thick on a tray which does not absorb moisture from the sample or cause contamination and then dried in oven at maximum temperature of 40 °C. Table 4. shows the amount of moisture removed from specific sample casseroles and the average for all its samples.

Table 4. Drying performance of Kraft lignin.

Drying performance		Before		After		
Casserole	m_{cass} [g]	$m_{cass+samp}$ [g]	m_{samp} [g]	$m_{cass+samp}$ [g]	m_{samp} [g]	Moisture removed [wt%]
1	25.70	935.40	909.70	613.30	587.60	35.41
2	25.80	929.50	903.70	607.70	581.90	35.61
3	25.50	962.40	936.90	627.70	602.20	35.72
4	30.10	905.60	875.50	592.40	562.30	35.77
5	29.70	892.30	862.60	583.00	553.30	35.86
6	25.30	996.00	970.70	649.00	623.70	35.75
7	29.80	959.50	929.70	626.50	596.70	35.82
8	30.20	904.30	874.10	591.20	561.00	35.82
9	30.20	947.80	917.60	619.10	588.90	35.82
10	25.60	893.60	868.00	582.80	557.20	35.81
11	25.90	920.40	894.50	601.10	575.20	35.70
AVG.			903.91		580.91	35.73
						Casserole = cass
						Sample = samp

After drying the Kraft lignin is mixed together and stored in a closed container. Figure 4. shows dried Kraft lignin that is stored in closed container.

Figure 4. Dried Kraft lignin.

5.1.2 Pyrolysis of Kraft lignin

Pyrolysis is performed to carbonize Kraft lignin to a biochar using Nabertherm HT furnace. The pyrolysis is performed in nitrogen-rich atmosphere by feeding 2 liters of nitrogen per minute throughout the pyrolysis. Continuous feeding of nitrogen is needed since the furnace in which the pyrolysis is carried out is not airtight. The lignin sample is placed in a graphite vessel with a lid. The graphite vessel is then placed into a bigger corundum vessel that is filled with graphite powder for preventing the biochar from reacting with oxygen. The temperature is then raised by 5 °C/min until the desired temperature is reached. When the temperature is reached, the sample is held for 4 hours after which the temperature is allowed to settle back to room temperature. Execution temperatures are 600 °C, 900 °C and 1200 °C. Table 5. shows the changes in mass and yield percentage for pyrolysis performed in different temperatures.

Table 5. Mass changes of Kraft lignin to biochar in pyrolysis.

Temperature [°C]	Mass of Kraft lignin [g]	Mass of biochar [g]	Yield percentage [%]
600	35.27	15.80	44.80
900	35.50	14.60	41.11
1200	35.51	14.69	41.37

During the pyrolysis, Kraft lignin changes state from powder to solid biochar which is hard but fragile containing some cracks. The coked Kraft lignin is extremely porous and

grinds easily. During this change its volume increases considerably despite its decreasing mass. Figure 5. presents pyrolyzed Kraft lignin.

Figure 5. Kraft lignin pyrolyzed at 1200 °C.

5.1.3 Grinding the sample

Grinding of the biochar is done by using Retsch ZM200 high speed centrifugal mill. The Retsch ZM200 uses impact and shearing forces between the rotor and a fixed ring to powder the materials gently and rapidly to the desired particle sizes. The size of rotors sieve determines the maximum size of the particle that will pass through to the collecting receptacle. Grinding sieve size of 0.5 mm is used to achieve maximum particle size of 0.5 mm. Grinding is performed to every sample and the biochar powder is stored for TGA tests. Figure 6. shows ground biochar powder.

Figure 6. Biochar powder.

5.1.4 Manufacturing of Kraft lignin briquettes

Manufacture of a briquette mixture starts by grinding the Kraft lignin using Retsch ZM200 so that its maximum particle size is 0.5 mm. After this a 10 wt.% of water is added to the dry Kraft lignin to increase its moisture content for briquetting. The Briquetting is done with an MKH 15k hydraulic press where 50 grams of Kraft lignin is placed in a steel mold with a diameter of 8.3 mm and pressed with force of 10 kN Applied force results a solid and hard briquette presented in Figure 7.

Figure 7. Manufactured Kraft lignin briquette.

5.1.5 Pyrolysis of Kraft lignin briquettes

The pyrolysis of Kraft lignin briquette is done similarly to dried Kraft lignin in chapter 5.1.2. Pyrolysis of Kraft lignin. The only exception is that briquette pyrolysis is carried out only in the maximum temperature of 1200 °C and not in 900 °C or 600 °C. Before the pyrolysis Kraft lignin briquette is fully solid and compact but can easily be chipped. After pyrolysis, the Kraft lignin briquette swells to form a hard but porous material that resembles Kraft lignin material previously pyrolyzed from the powder Kraft lignin. Pyrolyzed Kraft lignin briquette presented in Figure 8.

Figure 8. Kraft lignin briquette pyrolyzed at 1200 °C.

5.2 Experimental procedure and apparatus

TGA tests are done with NETZSCH STA 449F3 Jupiter® unit. This unit has TGA and DSC possibilities but in this study only TGA possibilities are used. Before TGA runs with the samples a baseline run is done to measure the static error so that it can be subtracted from the results obtained. The TGA test is performed for each pyrolysis sample according to Table 6.

Table 6. Summary of all experiments performed.

		Pyrolysis sample				
		1200	900	600	Coke	Briquette
TGA Tests	1250 °C	X	X	X	X	X
	1300 °C	X	X	X	X	X
	1350 °C	X	X	X	X	X

The start of the test is carried out in a 100 % nitrogen atmosphere for 100 mg samples. The sample is preheated to an initial temperature of 28 °C where it is kept for 2 hours so that nitrogen has time to fully displace the oxygen. After preheating, the sample is heated 10 degrees per minute to the desired temperatures. The target temperatures used in this study are 1250 °C, 1300 °C and 1350 °C. After reaching the target temperature, the protective nitrogen atmosphere is chanced to reactive gas atmosphere. The reactive

gas atmosphere contains 25% of carbon monoxide (CO), 25% of carbon dioxide (CO_2) and 50% of nitrogen (N_2). The change of atmosphere takes place over a period of 15 minutes, after which the sample is kept at the target temperature for 60 minutes. After holding, the TGA sample is allowed to cool down to the room temperature, before the next sample. The test is repeated for all samples.

5.3 TGA data obtained from the tests

Figure 9-11. shows the raw data obtained from a 1250 - 1350 °C TGA runs, where the blue line represents a biochar sample prepared at 600 °C, light green at 900 °C, and-, red at 1200 °C. Dark green curve represent briquette sample and the light blue line metallurgical coke sample. Rising dashed line shows the change in temperature which is identical for all the samples in the same figure and black dashed line shows the flow of nitrogen. The colors are shown in more detail in the Table 7. In Figure 11 there is a measurement error that has occurred at the beginning of the brick sample (dark green line). This error is due to the hardware error and it can be ignored.

Table 7. Line colors of the samples.

Sample	
600	
900	
1200	
Coke	
Briquette	
Temperature	
Nitrogen	

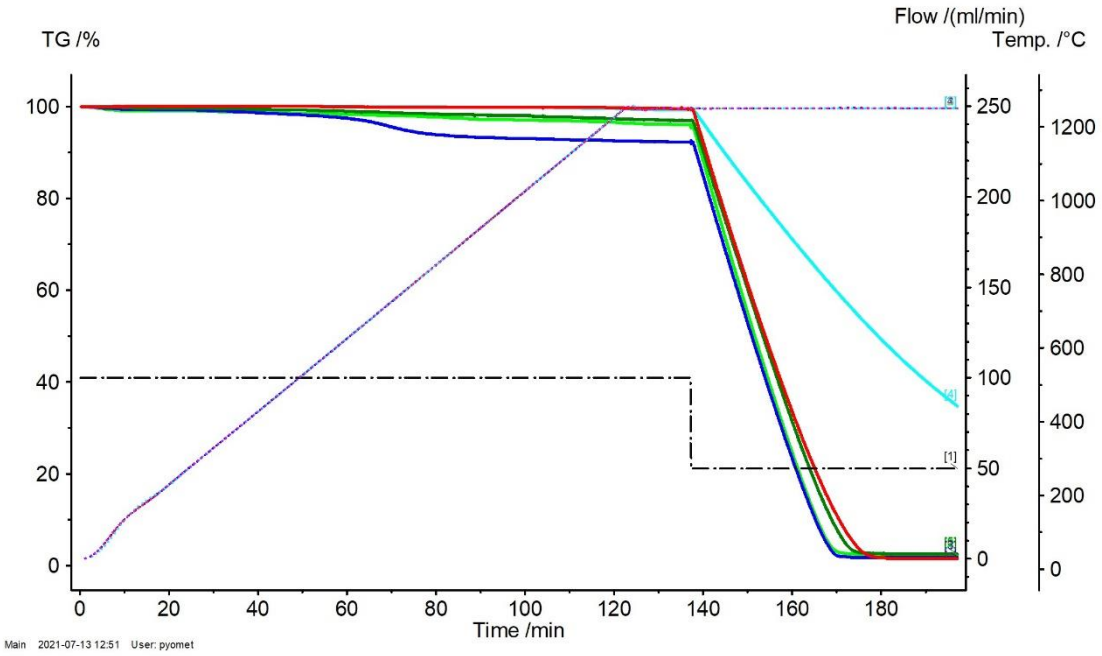

Figure 9. TGA data from a 1250 °C run.

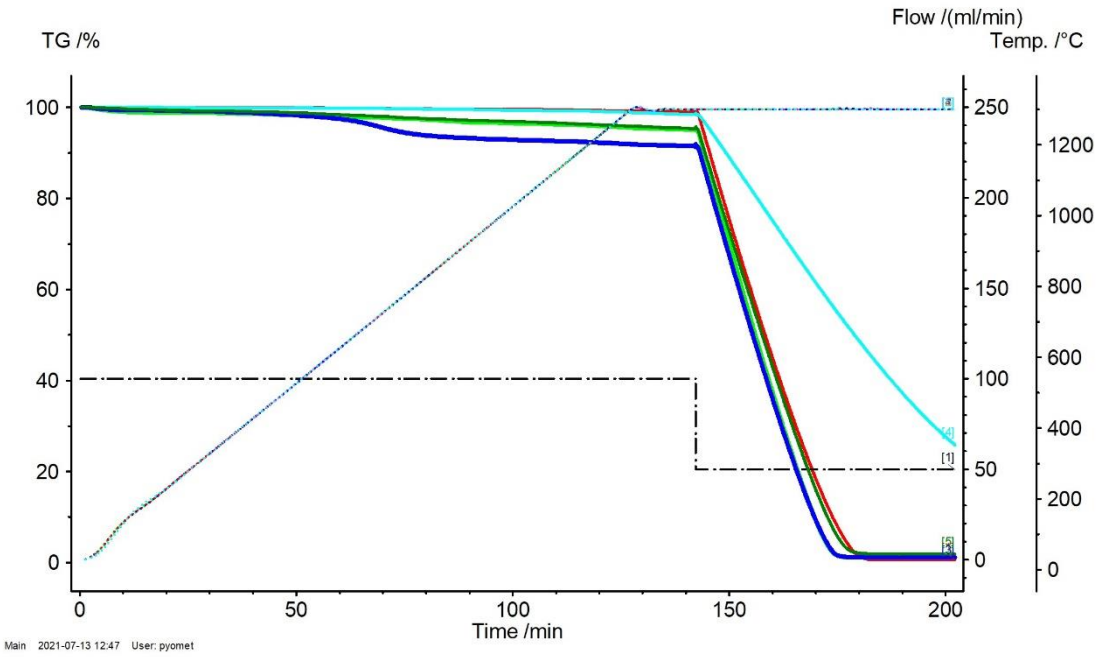

Figure 10. TGA data from a 1300 °C run.

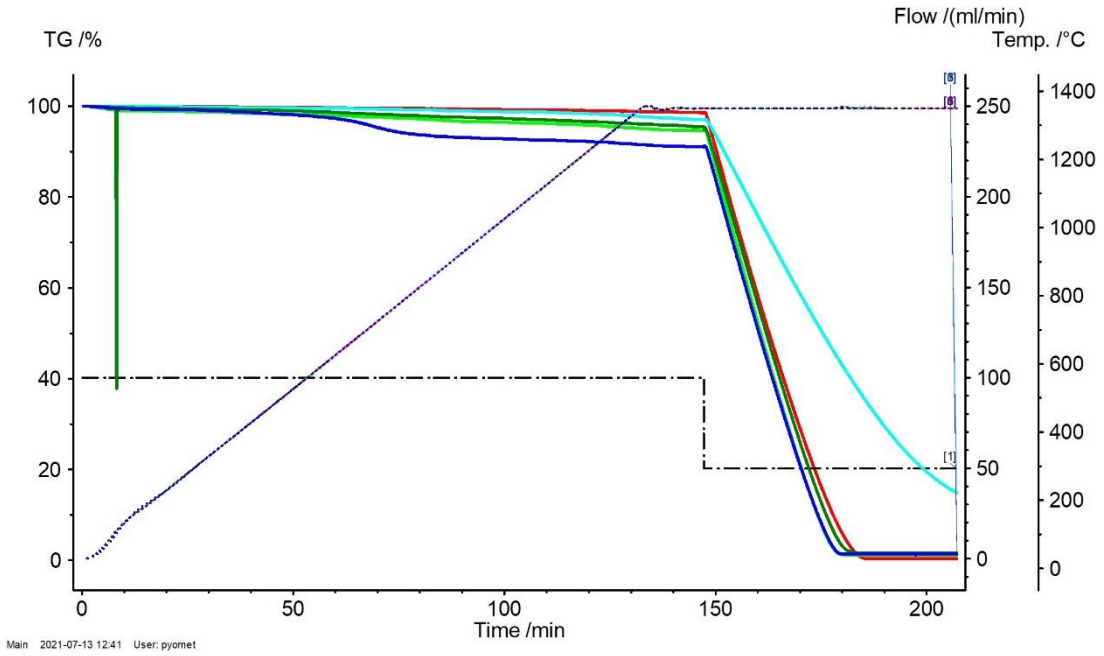

Figure 11. TGA data from a 1350 °C run.

From the Figures 9-11. can be seen that ones the reaction atmosphere is added the mass change starts to occur. The change in mass occurs from the reaction of carbon to carbon monoxide. The mass change of biochar is significantly faster than that of metallurgical coke, which is expected due to the more reactive nature of biochar. However, some of the change in mass occurs even before the actual drop, due to the sample preparation temperature. The lower the temperature at which the pyrolysis of the biochar samples is carried out, the more volatile constituents remain. When the temperature is raised above the pyrolysis temperature, the non-volatile constituents begin to evaporate, resulting in a mass change before reaction atmosphere being present. This is why for example the mass of biochar sample prepared at 600 degrees (blue line) starts to slowly drop down before the larger change in mass.

5.4 Determination of kinetic parameters

5.4.1 Reaction models applied to describe the thermal transformations in solids

The aim of the results is to determine the activation energy E_A generated for each TGA run, which can be used to form a kinetic model that predicts the gasification behavior of biochar at high temperatures. For this we had to conclude the best fitting reaction models. After several reaction model tests, we concluded that four of the best models

were power law, one-dimensional diffusion, contracting sphere and contracting cylinder models presented in Table 8. Figure 12. presents these models and their slope coefficients. The slope coefficient of the most ideal model would get value of 1 for the R^2 but in our case the best results are produced by the model of a contracting cylinder. The contracting cylinder model is reasonable because our TGA tests are done in a cylindrical container which may affect the gasification and be the reason why the model is more fitting than for example model of a contracting sphere.

Table 8. Most fitting reaction models. (Vyazovkin et al. 2010)

N	Reaction model	f(x)
1	Power law	$2/3x^{-\frac{1}{2}}$
2	One-dimensional diffusion	$1/2x^{-1}$
3	Contracting sphere	$3(1-x)^{\frac{2}{3}}$
4	Contracting cylinder	$2(1-x)^{\frac{1}{2}}$

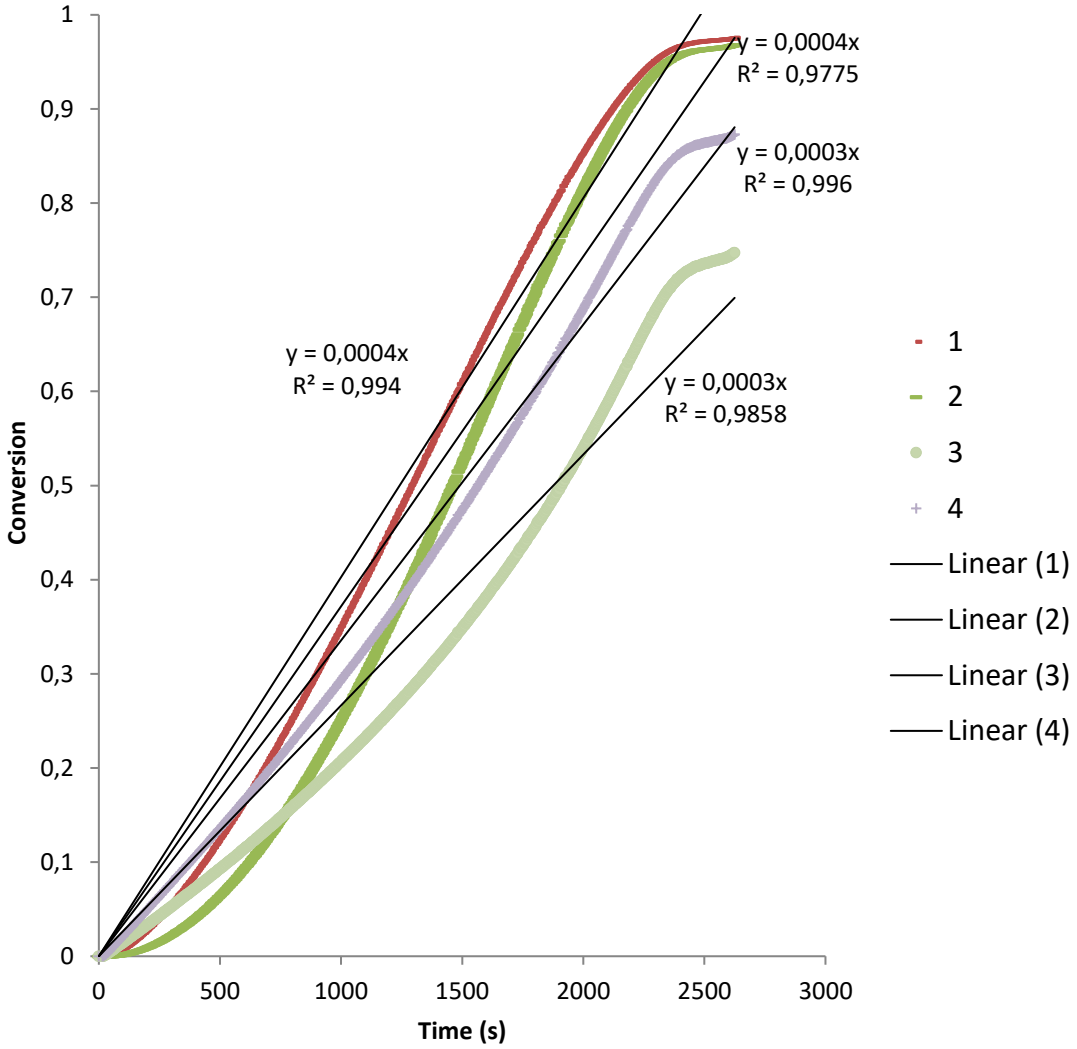

Figure 12. Compared reaction models and their slope coefficients.

Basic expression for the time derivative of the rate constant depended on partial pressure that is represented equation (9):

$$\frac{dx}{dt} = kp_{Co_2} f(x) \tag{9}$$

Where p_{Co_2} is the partial pressure of carbon dioxide and k is obtained by the Arrhenius equation, which is represented in equation (2)

When model of a shrinking cylinder is added to the equation (9) following equation (10) is obtained:

$$\frac{dx}{dt} = kp_{Co_2} 2(1-x)^{\frac{1}{2}} \tag{10}$$

This equation can be also presented different form in equation (11):

$$1-(1-x)^{\frac{1}{2}} = kp_{Co_2} t \tag{11}$$

where the variable x can be solved using the following equation (12):

$$x = 1-\left(1-k_0 e^{\left(-\frac{E_A}{RT}\right)} P_{Co_2} t\right)^2 \tag{12}$$

5.4.2 Processing of research data

From the TGA data obtained, the main focus is in the area where the change of the conversion is at its highest. The conversion from the sample mass to the volatile gases starts to occur when the target temperature is reached and reaction gases are added to the atmosphere, causing the samples to react to form carbon monoxide, resulting in a decrease in sample mass. When there is no excess oxygen in the reaction, the reaction equilibrium is one-sided and only carbon monoxide is formed. Gasification of solid carbon to carbon monoxide in the presence of carbon dioxide can be expressed as follows (13):

$$C_{(s)} + CO_{2(g)} \rightarrow 2CO_{(g)} \tag{13}$$

The progression of conversion is depicted in Figure 13. which shows a graph of the total TGA run from time 0 to the end of the test for a biochar sample prepared at 1200 ° C. From the graph, it can be observed that the area where the change in conversion is greatest (at time between 8000-11000 s). The conversion of the samples continues close to the value of 1, at which point conversion can be assumed to be completed.

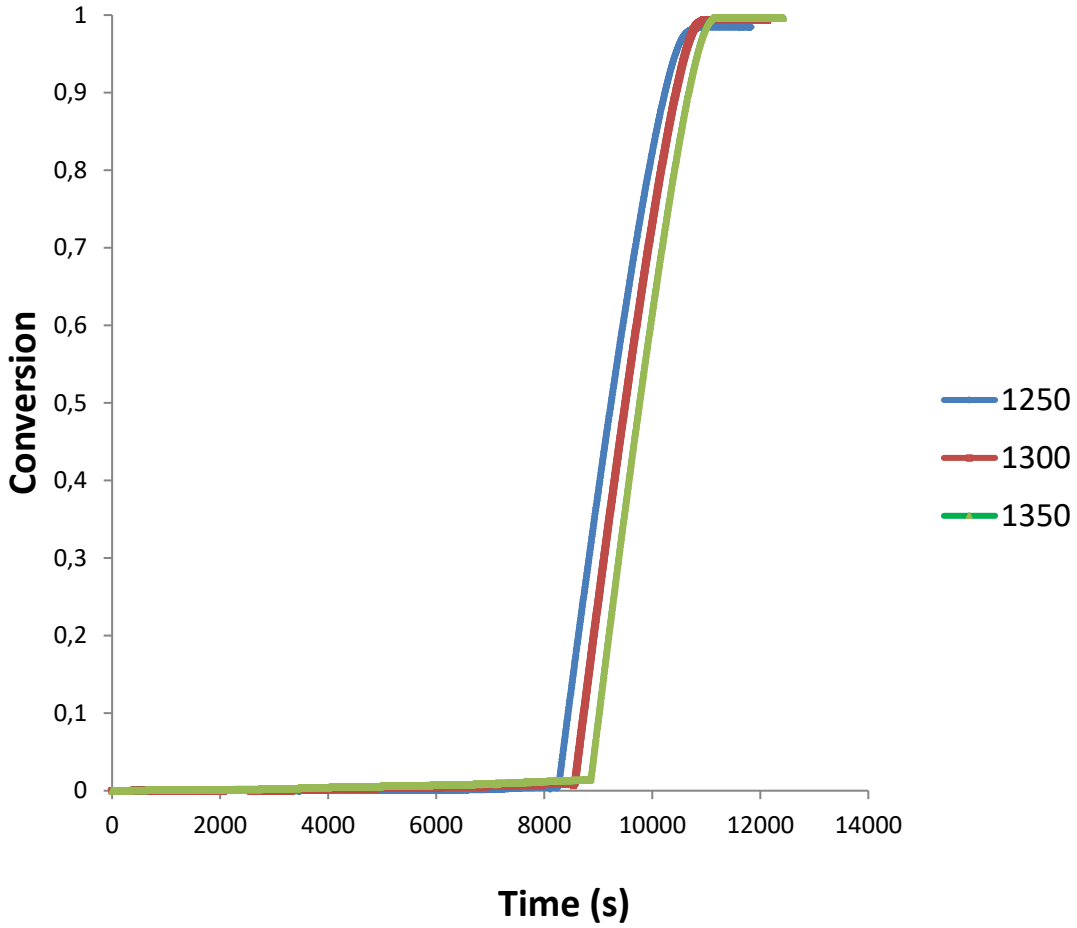

Figure 13. Conversion for the biochar sample prepared at 1200 °C.

In the calculation of the activation energy, we focus on the part where the progression of conversion is the greatest. This is presented in Figure 14. where each of the TGA run samples, a conversion slope is defined so that the Arrhenius graph can be determined.

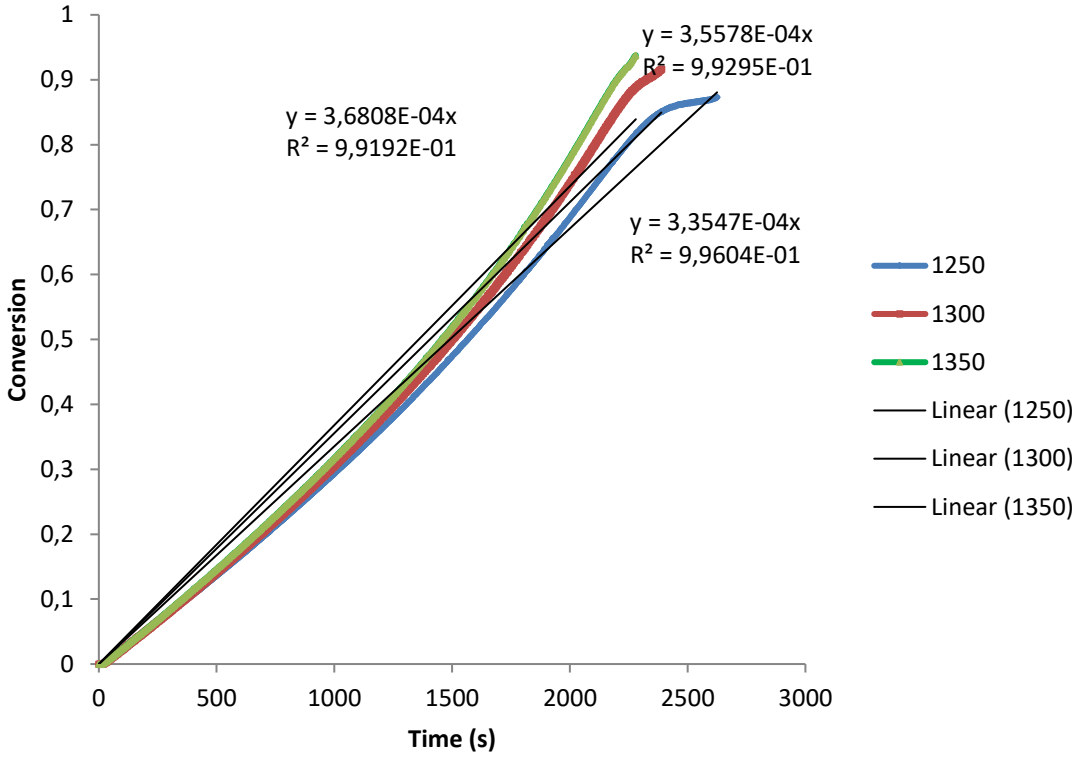

Figure 14. The modelled carbon conversion of biochar prepared at 1200 °C.

Using the slope from the generated Arrhenius graph presented in Figure 15. we can determine the values $-E_A/R$ and ln(k0), from which the values of E_A and k0 can be calculated directly.

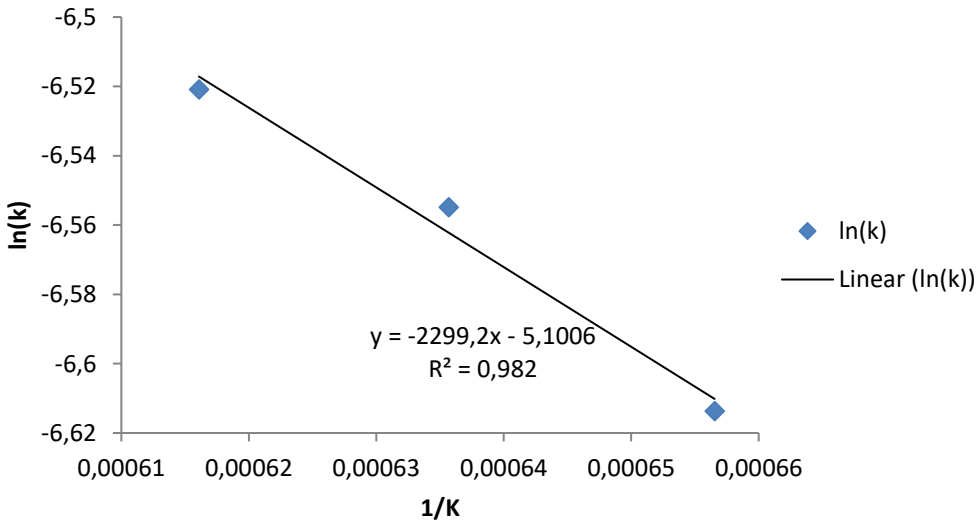

Figure 15. Arrhenius-plot for biochar sample prepared at 1200 °C.

The activation energy is calculated for each of the samples. The results of the activation energy are collected in Table 9.

Table 9. Activation energy of all the samples.

	Activation Energy (EA)	Speed constant (k0)
Pyrolysis sample	KJ/mol	1/s
1200 °C	19.1	0.00609
900 °C	11.2	0.00380
600 °C	6.6	0.00262
Coke	80.9	0.26503
Briquette	19.0	0.00617

Figures 16-20 shows the differences of measured and modelled values. The closer graph lines of the measured and modeled data, the better the model is to able to predict the kinetic values.

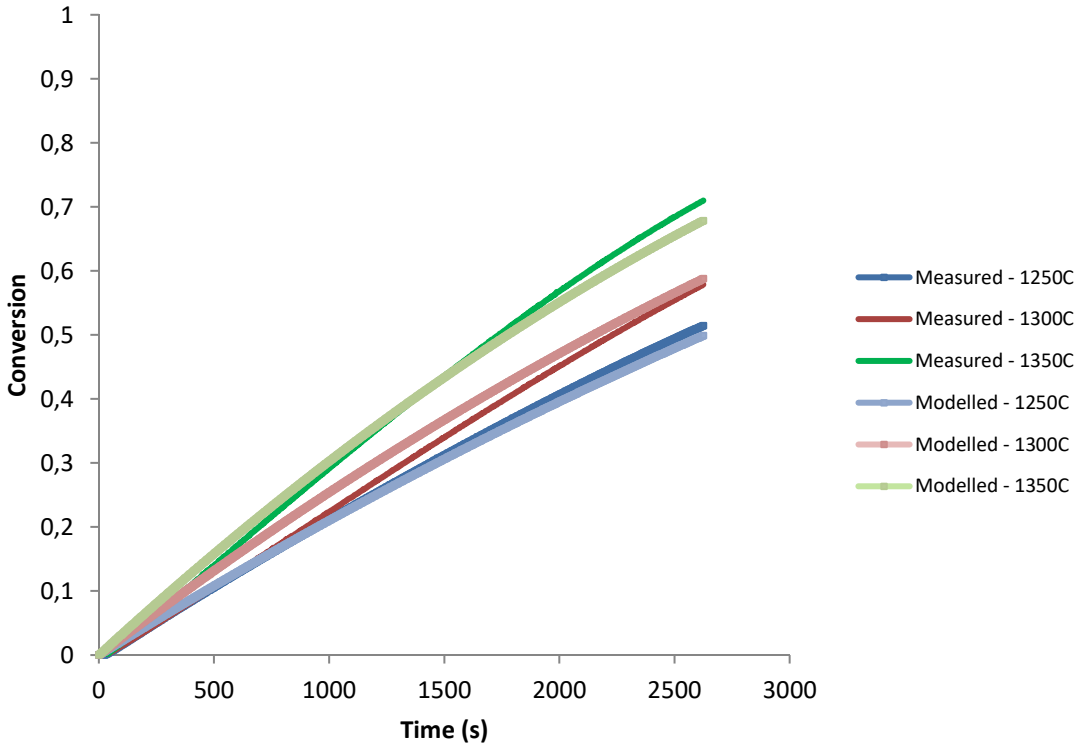

Figure 16. The measured and modeled values for the coke samples.

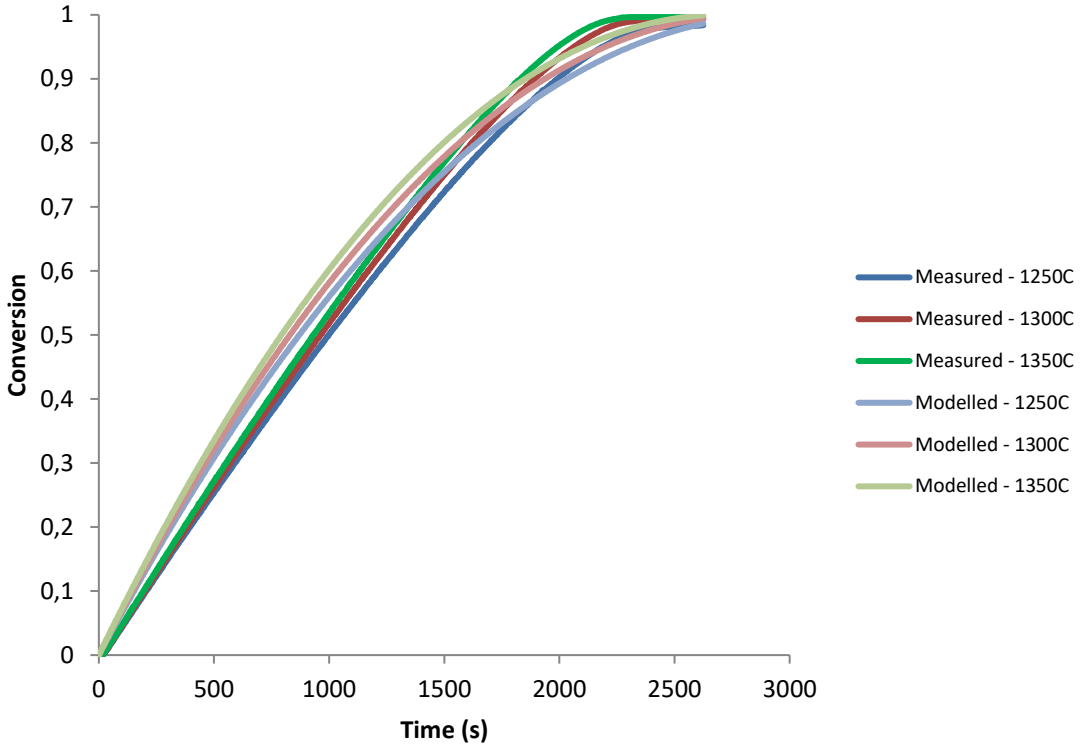

Figure 17. The difference between the measured and modeled values for the 1200 °C samples.

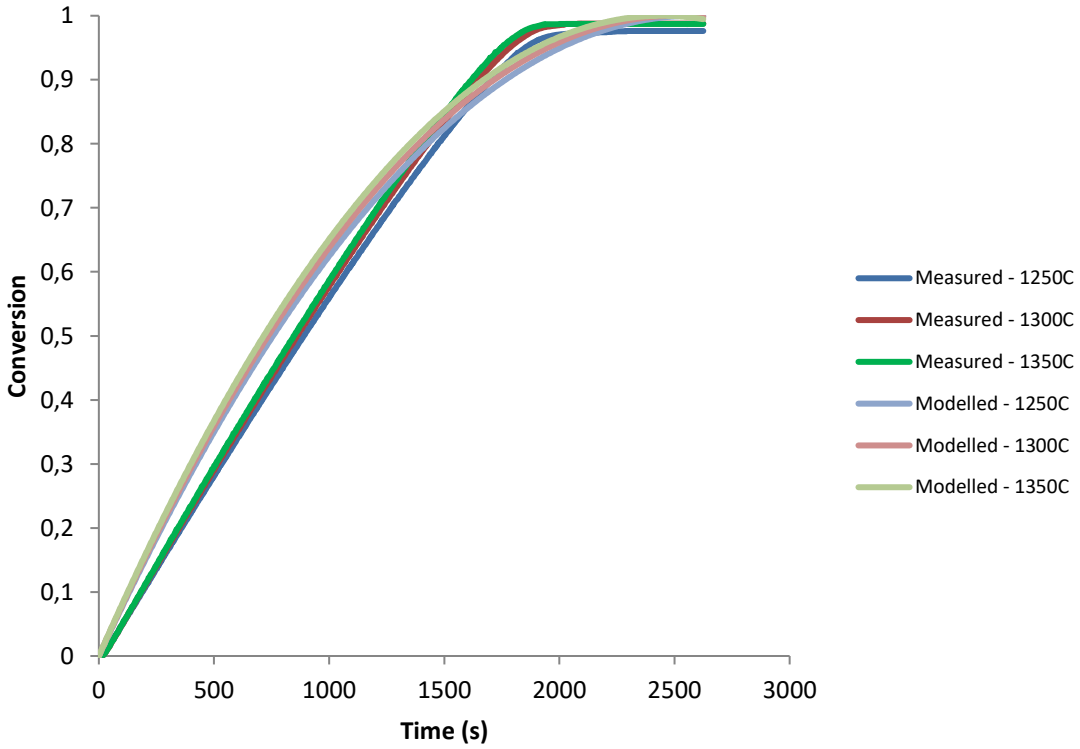

Figure 18. The difference between the measured and modeled values for the 900 °C samples.

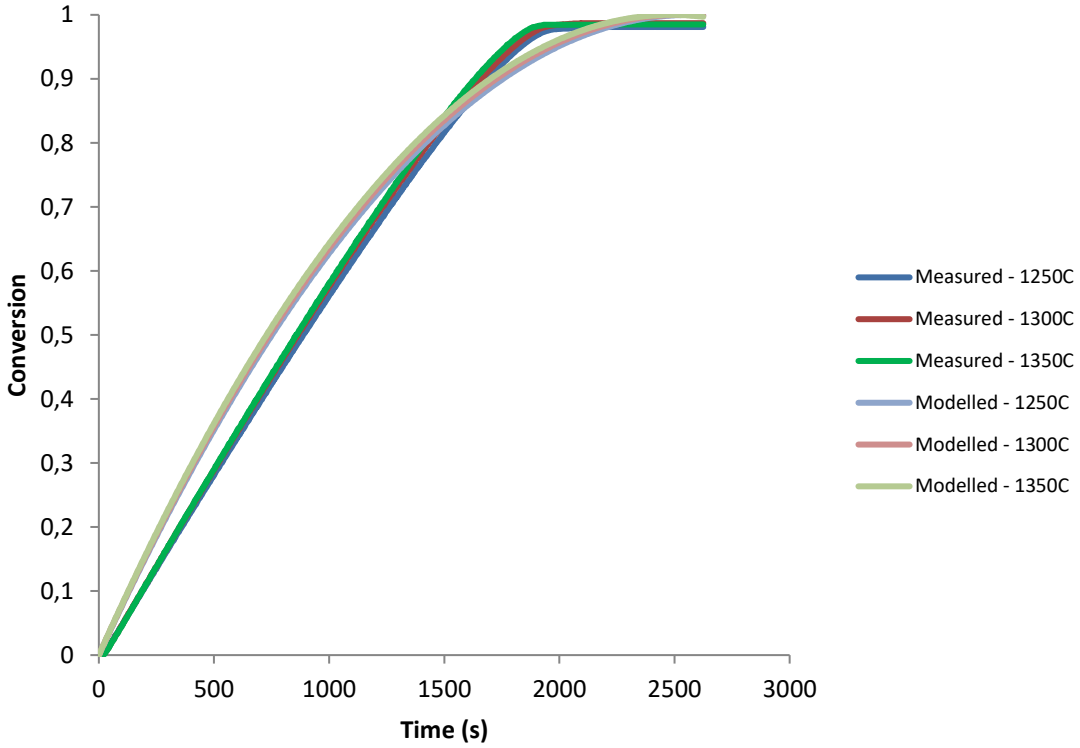

Figure 19. The difference between the measured and modeled values for the 600 °C samples.

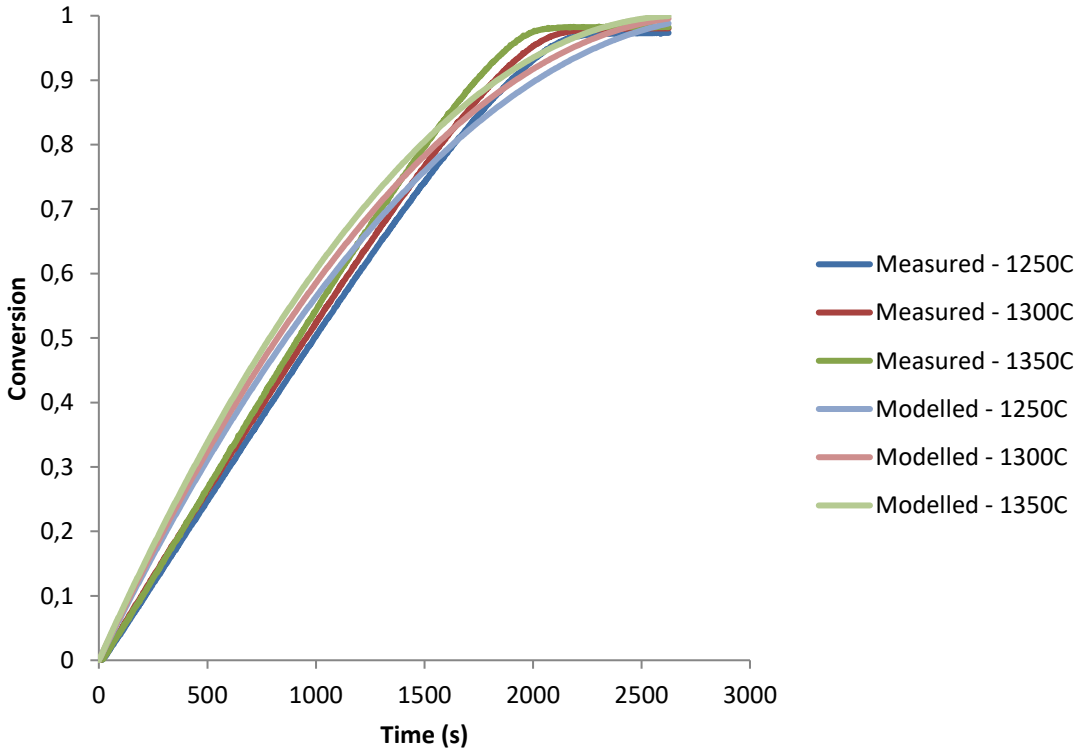

Figure 20. The difference between the measured and modeled values for the briquette samples.

5.5 Discussion

5.5.1 Suitability of the kinetic model

When comparing the measured and theoretical data from the contracting cylinder model, the suitability of the kinetic model can be verified. From the Figures 16-20. can be seen that in the measured data, the change in conversion with respect to time is more linear and reaches the maximum faster than the theoretical model. This means that the measured gasification happens on average slightly faster than the model can predict. The reason could be that in modelled contracting cylinder model the gasification is assumed to occur faster at the surface of the cylinder in comparison to its interior. The outer surface can be assumed to protect the inner part from gassing, which is why the conversion rate is predicted to be higher at the beginning of the gasification and slows down at the end. In our tests the 1200 °C, 900 °C and 600 °C samples, the biochar is in powder form, which makes gasification easier than for example in a cylindrical pellet where the inner part is harder to access. However, the differences are small and the modelled and measured data are close to each other and because of that it can be said that the contracting cylinder model is well suitable for the prediction of kinetics of gasification reaction of biochar and metallurgical coke samples.

5.5.2 Compatibility of the obtained values with the literature

There are several studies in the literature investigating the gasification kinetics of coal and biochar. Table 10. shows the results obtained from the literature for various gasification experiments implemented. From this it can be seen that the value of the activation energy varies a lot. At its maximum, the activation energy can get values more than 200 kJ/mol, while at its lowest the values are around 40 kJ/mol. However, the value of the activation energy is highly dependent on many factors like the kinetic model used, particle size, pressure, atmosphere, and the material used. Therefore, the activation energy cannot be directly and reliably compared without considering the above-mentioned variables.

Although the activation energies from the gasification of Kraft lignin biochar are very small (6-19 kJ/mol) when the variables are considered the magnitudes of the values obtained from the gasification experiments are in realistic order of magnitude.

Table 10. Results of gasification kinetics for coal and biochar from literature. (J. Chen et al. 2019; Pearson 1976; Liu et al. 2017; Xu, Wu, and Bhattacharya 2021; Tang, Wu, and Wang 2015; Preciado-Hernandez et al. 2021; Park and Ahn 2007)

Material	Atmosphere	Kinetic model	Particle size	Temperature range	Activation energy	Rate constant
Maddngley char (1)	CO2 (30-90%)	Modified volumetric model	20-106 µm	750-1100 °C	219-220 (kJ/mol)	2.27×10^{9} - 2.74×10^{9} (1/min)
Yallourn char (1)	CO2 (30-90%)	Modified volumetric model	20–106 µm	750-1100 °C	197-208 (kJ/mol)	1.99×10^{8} - 5.62×10^{8} (1/min)
Kentucky Bituminous coal (2)	CO2 (25%)	Random pore model	200 µm	950-1150 °C	45.8 (kJ/mol)	3.43×10^{-5} - 6.43×10^{-5} (1/min)
Kentucky Bituminous coal (2)	CO2 (25%)	Random pore model	200 µm	950-1150 °C	82.4 (kJ/mol)	3.57×10^{-5} - 1.112×10^{-5} (1/min)
Brazilian mineral coal (3)	H2, CO, C02	Shrinking core model	-	800-1000 °C	165 (kJ/mol)	1.3×10^{-5} – 23.5×10^{-5} (1/min)
Brazilian mineral coal (3)	H2, CO, C02	Continuous Model	-	800-1000 °C	165 (kJ/mol)	0.022 - 0.414 (L/min)
Bituminous coal char (4)	Co2, H2O, CO, H2, N2	Un-reacted shrinking-core model	1.5 mm	900–1100 °C	47.06 (kJ/mol)	0.00531 - 001094 (L/min)
Bituminous coal char (4)	Co2, H2O, CO, H2, N2	Un-reacted shrinking-core model	1.5 mm	900–1100 °C	95.53 (kJ/mol)	5.15×10^{-4} - $2{,}11\times10^{-3}$ (1/min)
Yuxi lignite (5)	CO2, CO, CH4	Active site/intermediate model	<0.17 mm	675-950 °C	71.86 (kJ/mol)	83.44 (1/min)
Xundian coal (5)	CO2, CO, CH4	Active site/intermediate model	<0.17 mm	675-950 °C	119.2 (kJ/mol)	1.11×10^{-7} (1/min)
Tyre pyrolysis char (6)	H2O, N2	Volumetric model	~71.46 µm	750–950 °C	114.3 kJ (kJ/mol)	5.42×10^{-3} (1/s)
Alaska char (7)	CO2	Shrinking particle model	45-63 µm	850-1000 °C	215 (kJ/mol)	9.37×10^{-7} (1/min)
Cyprus char (7)	CO2	Shrinking particle model	45-63 µm	850-1000 °C	194 (kJ/mol)	1.22×10^{-7} (1/min)
Drayton char (7)	CO2	Shrinking particle model	45-63 µm	850-1000 °C	223 (kJ/mol)	1.05×10^{-8} (1/min)
CNCIEC (7)	CO2	Shrinking particle model	45-63 µm	850-1000 °C	149 (kJ/mol)	5.17×10^{-4} (1/min)
Denisovsky (7)	CO2	Shrinking particle model	45-63 µm	850-1000 °C	199 (kJ/mol)	6.31×10^{-6} (1/min)

Table 11. References in Table 10.

Sources	
(1)	(Xu, Wu, and Bhattacharya 2021)
(2)	(Liu et al. 2017)
(3)	(Pearson 1976)
(4)	(J. Chen et al. 2019)
(5)	(Tang, Wu, and Wang 2015)
(6)	(Preciado-Hernandez et al. 2021)
(7)	(Park and Ahn 2007)

5.5.3 Error evaluation and areas for improvement

This work has been completed over a period of six months, which has resulted in limited sample sizes. In order to increase the accuracy of the test results, it is possible to increase the sample size and the number of tests performed on the samples. For example, by performing more TGA runs at different temperatures, it is possible to obtain more data points for the Arrhenius plot and thus more accurate activation energies as well as reaction rate constants. Also, pressure monitoring and gas analysis of TGA tests could give more accurate picture of the overall situation.

In the future, the accuracy can also be improved by considering the amount of ash in the samples as well as the analysis of other impurities. In this work, the amount of ash has not been measured or taken into account in calculations, regardless of its presence. In addition to this, it would be good to look at the lengths of the different experiments. Although all the other tests were the correct lengths, in the TGA experiments for the coke the conversion did not reach the end before the experiment was over and therefore, the accuracy of the coke activation energy result can suffer more error when compared to others samples. More compressive force could also be used to make the briquette sample, as the briquette did expand during pyrolysis.

In theory, it is also possible to use a better kinetic model, as a small error arises from the use of the model used. However, finding a better model requires a considerable amount of work and, in some cases, even the development of an entirely new model just for this specific work. Overall, the magnitude of errors in this work are relatively minor and it

can be stated that if the experiments were repeated, the results would be of the same order of magnitudes.

5.5.4 Future follow-up studies

In future research related to the kinetics of gasification of biochar made of Kraft lignin the focus could be more on the effects of the briquette. The compression of the Kraft lignin briquette could possibly be done with higher force than in this study or be done to the already pyrolyzed Kraft lignin biochar. Also, the function of various binder materials such as Kraft lignin itself in the manufacture of briquettes would be a good subject for further research. Once the optimal way to produce Kraft lignin briquette is known its effect on gasification kinetics would be an excellent information in future applications.

Also, a focus on the practicality of Kraft lignin biochar in an industrial environment might give some interesting information for the future. For example, measuring the strengths of the pyrolyzed Kraft lignin before/after grinding and investigating the effect of different concentrations of ash and moisture in biochar would provide comprehensive information when considering future applications.

6 CONCLUSIONS

In this study, an investigation on the kinetics of gasification of biochar made of Kraft lignin is presented. The contracting cylinder model was found to be applicable for prediction of the gasification behavior of biochar and metallurgical coke. The error between the measured data and theoretical model was minor. The gasification conversion rate with biochar made from Kraft lignin did not increase significantly with different TGA temperatures. The pyrolysis temperature of the biochar pyrolysis was found to affect the gasification rate. The lower the pyrolysis temperature of the biochar, the slower the gasification time but more gasification occurred in TGA tests.

The activation energy and rate constant values for all the biochar samples were between 6-19 kJ/mol and 0.00262-0.00617 1/s depending on the pyrolysis temperature. The lower the pyrolysis temperature in the preparation for the sample, the lower the activation energy (kJ/mol) and rate constant (1/s) values. The activation energy of metallurgical coke was around 80 kJ/mol and the rate constant of 0.26503 1/s which is significantly higher than that of the biochar. The magnitudes of activation energy and rate constant were as expected with coke and biochar. The Kraft lignin prepared as briquette did not hold its shape during the pyrolysis. As a result, the activation energy and rate constant received the same values as the otherwise identically prepared sample.

As a result of this study, it can be said that biochar made from Kraft lignin is a very reactive material with low values in activation energy and rate constant. When compared to the literature, these values are in between the expected magnitudes. In the future the use of biochar made from Kraft lignin in industry could be possible especially as long as its manufacturing costs and production volume problems has been solved.

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